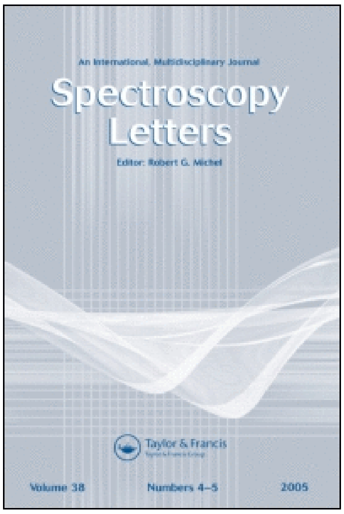

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Relative Sensitivity Factors for Rare Earth Elements in Different Matrices Employing Spark Source Mass Spectrometry

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RELATIVE SENSITIVITY FACTORS FOR RARE EARTH ELEMENTS IN DIFFERENT MATRICES EMPLOYING SPARK SOURCE MASS SPECTROMETRY

(Key words:Spark source mass spectrometry;Relative sensitivity factors(RSFs);Lanthanides;Computation of RSFs)

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ABSTRACT

Relative Sensitivity Factors(RSFs)for the rare earth elements Ce,Nd,Sm,Eu,Gd,Dy,Er, and Lu have been determined in U_3O_8-graphite and pure graphite matrices under similar experimental conditions employing Spark Source Mass Spectrometry(SSMS) with electrical detection system in magnetic peak switching mode. The RSF values differ very much when the matrix element(uranium in U_3O_8-graphite system or carbon in pure graphite) is the reference, But they show very good agreement when Er, one of the rare earth elements is chosen as internal standard.The literature data on RSF values for the rare earth elements in Y_2O_3 as well as Al matrices are compared with those obtained in the present work. An attempt has been made to explain the similar trend in the RSF

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values in all these matrices in terms of the decomposition pattern of the rare earth oxides. An empirical equation relating the RSFs with the decomposition energies of the lanthanide sesquioxides and monoxides has been shown to be useful in computing the RSFs for the lanthanides in various matrices.

INTRODUCTION

The quantification of measurements in Spark Source Mass Spectrometry(SSMS) involves the determination of Relative Sensitivity Factors (RSFs) which depend on the trace constituent,the matrix and the sparking conditions as well as the detection systems employed. The RSFs for the rare earth elements Ce,Nd,Sm,Eu,Gd,Dy,Er,and Lu in U_3O_8,the starting material for the nuclear fuels have been reported from this laboratory$^{(1)}$. High purity graphite powder has been used as conducting material for U_3O_8 sparking. In view of the low specification limits for these elements in uranium oxide it is essential to correct for the blank contribution from graphite. Moreover graphite itself is an important material in nuclear technology as it is used as neutron reflector in nuclear reactors.It's purity with respect to neutron absorbing materials should therefore be establisned. It was therefore considered worthwhile to determine the RSFs for the rare earth elements in graphite matrix.

This paper gives the details of the experimental work and compares the RSFs obtained in graphite matrix with those in U_3O_8-graphite system$^{(1)}$, uranyl nitrate$^{(2)}$, as well as in $Y_2O_3$$^{(3,4)}$ and Al$^{(5)}$ matrices. Such a comparison of RSFs has been reported in the case of other elements$^{(6)}$, but no such thing is known to have been done for rare earth elements so far. Comparing RSFs in different matrices is helpful in deducing empirical relationships for computing RSFs which is useful in the event of nonavailability of reference standards for trace constituents especially in nuclear materials.

EXPERIMENTAL

Apparatus

The instrument used in the present work was a JEOL JMS 01BM-2 double focusing mass spectrometer with Mattauch-Herzog geometry. The details of the instrument have been described earlier(1).

Preparation of synthetic samples

The procedure adopted for the preparation of U_3O_8 synthetic samples containing known amounts of rare earth elements is described elsewhere(1). For the preparation of graphite synthetic samples the following procedure was adopted. A known amount of high purity graphite was wetted with sufficient amount of acetone. Known amount of a grand mixture of rare earth nitrate in which the concentration of each rare earth element was known was then added into graphite. The mixture was swirled and then subjected to ultrasonics for 30 min. Then acetone was evaporated gently by passing hot air over graphite. Final drying was carefully done under infrared lamp. The powder was ground and taken for electrode preparation.

Mass spectrometric procedure

The synthetic samples were directly molded in the form of electrodes using a hydraulic press at a pressure of $110 Kg/Cm^2$ for about 20 minutes. After fixing the electrodes in the ion source, the sample positioning jig was used to allign the electrode gap in the line of the acceleration slit. Final adjustment of the configuration for the maximum ion transmission was carried out by alligning the electrode gap, the acceleration slit and the main slit along the ion optics geometry. The electrodes were presparked for about 5 minutes to remove any surface contaminants. The experimental conditions are summarised in Table 1.

TABLE 1. Sparking conditions employed in the experiments

Power Amplifier Anode Voltage	2.5 K.V
Pulse width	20 μS
Pulse repetition frequency	1 KHz.
Acceleration voltage	25 K.V
Electrostatic field	2.5 K.V
Main slit	200 μm.
α and β slits	1.5 mm.
Collector slit	200 μm.

Electrical detection system in peak switching mode was employed and the rare earth isotopes monitered were ^{140}Ce, ^{143}Nd, ^{147}Sm, ^{152}Sm, ^{153}Eu, ^{160}Gd, ^{163}Dy, ^{166}Er, ^{175}Lu, and ^{13}C. The ion currents corresponding to these isotopes were integrated in different channels keeping a preset value (0.3 or 1 nC)for the total ion monitor. Time taken for each integration was about 15 to 20 seconds. The concentration of the trace constituent was directly obtained in ppmw on a HP 9815-S desk-top calculator.

RESULTS AND DISCUSSION

Precision

The RSFs for the rare earth elements in U_3O_8-graphite system as well as in pure graphite matrices with respect to the corresponding matrix element(U in U_3O_8-graphite system or C in pure graphite) as reference are shown in Table 2.

An overall precision of about 10% was obtained in U_3O_8 whereas it was about 17% in the case of graphite matrix. It may be mentioned that while preparing the U_3O_8 samples, the 'solution route' namely the mixing of lanthanides taken in nitric acid with uranyl nitrate solution and converting into oxides by calcination was adopted. This method has been shown to be the best and capable of giving

TABLE 2. RSFs for rare earth elements in U_3O_8 and graphite matrices. Matrix element is reference.

Element	U_3O_8-graphite	Pure graphite
Ce	1.53±0.13*	8.15±1.30*
Nd	1.72±0.21	12.10±1.22
Sm	1.90±0.26	12.37±1.85
Eu	1.93±0.28	12.63±2.86
Gd	1.42±0.03	9.23±1.09
Dy	1.64±0.07	11.63±2.03
Er	1.54±0.12	11.01±1.81
Lu	1.36±0.06	7.89±1.86

* Indicates standard deviation at 1σ(67% confidence)level

reproducilibility of about 7%(4). As regards to graphite, because of it's insolubility, semi dry blending method was adopted. This method of preparation of samples is expected to give reproducibilities of about 20%(7). As the experimental conditions during the SSMS analysis in both the samples were maintained identical, the large imprecision in RSFs in graphite matrix may therefore be attributed to the limitations in the preparation of homogeneous samples.

Correction for the blank contribution

Once the RSF values for the desired elements are known in U_3O_8 as well as in graphite matrices, the correction for the blank contribution from graphite is effected as follows:

Let T_U be the concentration of a trace constituent T, per gram of U in U_3O_8 and T_C be it's concentration in graphite. If χ g of U_3O_8 and y g of graphite are mixed for SSMS analysis, then the total amount of the trace constituent T in the resulting mixture is given by

$$\text{total amount} = 0.848\chi . T_U + y . T_C \qquad \text{-------(1)}$$

The factor 0.848 is introduced to convert the weight of U_3O_8 taken to that of uranium. Dividing through out by 0.848χ, we get

$$(T(\text{total}))^{U}_{U_3O_8:C} = T_U + y.T_C/0.848x \text{ ------------(2)}$$

Where the term on the left hand side of the equation is the total concentration of T per g. of U in U_3O_8:C system using U as the reference. If T_U^{obs} is the observed concentration of the trace constituent in U_3O_8:C and T_C^{obs} is the corresponding quantity in pure graphite, $(RSF)^T_U$ is the RSF of T with respect to U and $(RSF)^T_C$ is the RSF with respect to C , it follows that

$$(T(\text{total}))^{U_3O_8:C} = (T_U^{obs}/RSF)^{U}_{U_3O_8:C}$$

$$T_C = (T_C^{obs}\ /RSF)^C_C$$

Substituting these values in eqn.(2) the true concentration of the trace constituent T, corrected for blank

$$T_U = (T_U^{obs}/RSF)^{U}_{U_3O_8:C} - y/0.848x(T_C^{obs}\ /RSF)^C{}_C \text{ ------(3)}$$

Thus it is seen that the extent of blank correction depends on the weight ratios of U_3O_8 and graphite taken for electrode preparation and also on the RSF value of the trace constituent in both the matrices. Normally spec pure graphite (concentration of the trace elements present is less than 0.1 ppmw)is taken for mixing with U_3O_8,then blank correction becomes significant only if the trace constituent present in U_3O_8 is less than 0.1 ppmw in which case the correction comes to greater than 10%.

Comparison of the RSF values for lanthanides in U_3O_8 and graphite matrices

From the table 2 it is apparent that when the matrix element is the reference,the RSF values are different. The values in graphite matrix are by a factor of 6 to 8 larger than those in U_3O_8 matrix. With a view to understanding this large difference in the RSF values for lanthanides in U_3O_8 and graphite , individual contributions of the isotopes ^{13}C and ^{235}U to the total ionic charge were monitored. Though the atomic concentration of carbon was about 23 times more than that of uranium(for a 1:1 mixture by weight of U_3O_8 and graphite),experimentally it was found that the contribution from carbon ions to the total ion charge was only 4 times larger. The concentration of a trace constituent T when calculated is given by

$$T_U = \frac{(IM/TIM)_T}{y} \; \frac{0.72}{Atom\ \%} \; \frac{\langle At.Wt \rangle}{238.03} \qquad \text{-----} \; (4)$$

where y is the (IM/TIM) value for ^{235}U, 0.72 is the atom % abundance of ^{235}U and 238.03 is the the atomic weight of uranium. The concentration of the trace constituent with respect to carbon becomes

$$T_C = \frac{(IM/TIM)_T}{4y} \; \frac{1.01}{Atom\ \%} \; \frac{\langle At.Wt \rangle}{12} \qquad \text{-----} \; (5)$$

since (IM/TIM) for carbon is four times that of (IM/TIM) for ^{235}U. From the equations 4 and 5 it follows that

$$T_C = 7.T_U$$

showing the large influence of the matrix element on the concentration of the trace constituent. The difference in the (IM/TIM) values for ^{13}C and ^{235}U can be explained in terms of the difference in the energy distributions for both uranium and carbon ions in the rf-spark source. Further,in double focusing instruments a certain energy pass band in the ion beam is selected and ions having the energy distribution in this pass band only are allowed to pass into the analyser. For any given ion species,the fraction passing into the analyser depends on the shape of the energy distribution curve and the location of it's maxima with respect to the energy pass band. The maxima of energy distribution in uranium and carbon ions may not be the same and that of carbon may have been removed farther away from the energy pass band. Hence different fractions of these ions may be available in the energy pass band selected. This dependence of the energy distribution on the m/z of the element has also been observed by Van Hoye etal.(8) and Vos etal (9) Van Hoye etal.(10) also observed a rather large RSF value of 6 for lanthanum in steel with respect to the matrix element iron. In addition to the different energy distributions in the case of uranium and carbon, the tendency of carbon to form carbon clusters even upto C_{28}, results in the decrease of C^{+} ion intensity in the rf-spark leading to a reduction in (IM/TIM) value when compared with that of uranium. However, notwithstanding the difference, the same trend in the RSF values in both the matrices indicate that similar evaporation and ionisation processes of the lanthanides under the experimental conditions are occurring in all the matrices.

With Er as internal standard(11), the large difference in the RSF values vanishes as is seen from table 3. With a view to comparing the RSF values obtained in the present work with those available in literature, the RSF values reported by Carter etal(2) in uranyl nitrate, Sasamoto etal.(3) and Griffith etal.(4) in Y_2O_3 matrix and by Vanpuymbroeck(5) in Al matrix are given in the same table. The difference in the RSF values may be attributed to different sparking conditions employed and the detection systems used. It may be noted that the lanthanides are present as oxides in U_3O_8 and Y_2O_3 matrices while they are nitrates in uranyl nitrate, graphite and Al matrices. Among these only Carter's data show a different trend in RSF values. Figure 1 gives a graphical representation of the RSF values obtained in the present work as well as by others.

An attempt was made to understand the difference in the trend of RSF values between the present work and that of Carter etal in terms of the vaporisation processes in the case of oxides and nitrates. While discussing the RSFs for rare earth elements in U_3O_8, these authors reported (1) that the behaviour of rare earth elements can be explained interms of the decomposition energies of the sesqui-oxides or bond dissociation energies of the monoxides. Hence both in U_3O_8 and

TABLE 3. Relative sensitivity factors for the rare earth elements with Er as internal standard.

Element	Graphite present work	U_3O_8-C	Uranyl (2)nitrate	Y_2O_3 (3)^3	Y_2O_3 (4)^3	Al (5)
Ce	0.74	0.99	0.98	0.70	0.52	0.96
Nd	1.10	1.12	1.05	1.63	1.08	0.94
Sm	1.13	1.23	1.03	1.74	1.43	1.00
Eu	1.15	1.26	0.95	2.16	1.63	1.16
Gd	0.84	0.91	--	1.10	0.85	1.50*
Dy	1.06	1.06	--	1.16	1.10	0.97
Er	1.00	1.00	1.00	1.00	1.00	1.00
Lu	0.72	0.88	--	0.83	0.79	0.84

* Suspected contamination from oxides of La and Ce

Y_2O_3 matrices the trend in RSFs is same. As regards to the nitrates it was reported (12-14) that these nitrates decompose at relatively low temperatures as follows:

$$M(NO_3)_3.xH_2O \longrightarrow MONO_3 \longrightarrow M_2O_3$$

The step1 proceeds at a low temperature of about 70°C.while the second step occures at about 500°C. Even uranyl nitrate decomposes to U_3O_8 at this temperature Hence the formation of the metal ion is again from the decomposition of the metal oxide. It is therefore expected that the trend in RSFs should be same irrespective of nitrate or oxide matrix. It is indeed so in the case of Al and graphite matrices as seen from Figure 1. The deviation in Carter's data is thus difficult to explain.

Computation of RSFs:

The use of calculated RSF values assume importance when no reference materials are available for calibration. This is more so in

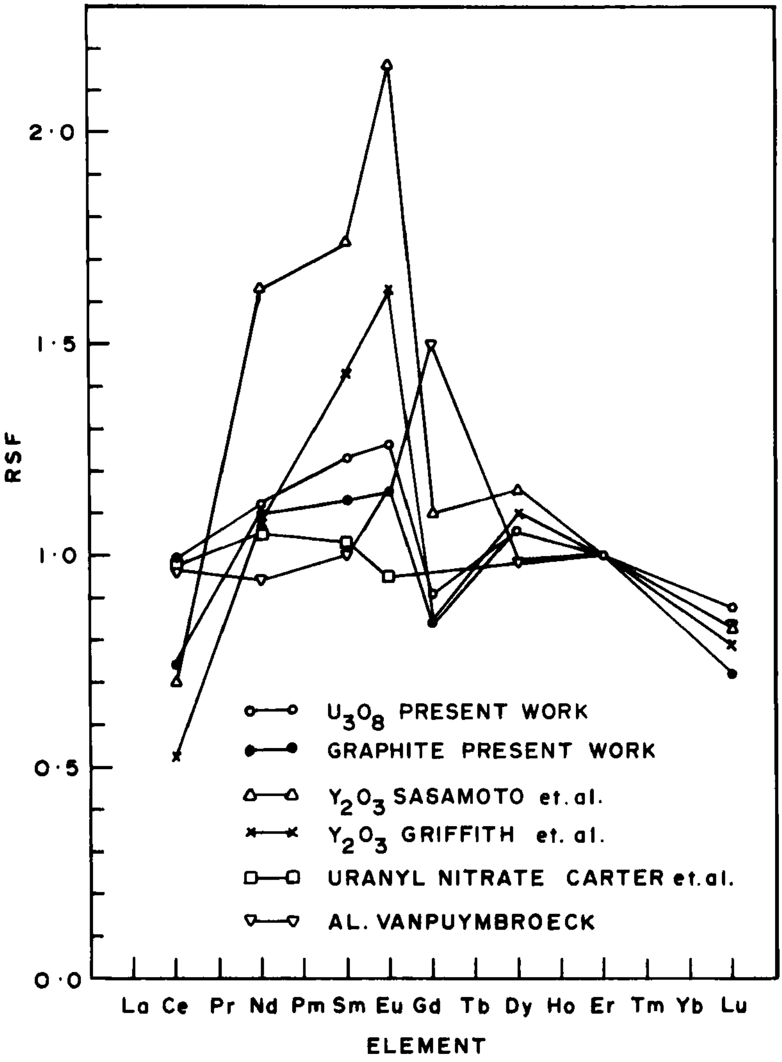

FIG.- 1 . RELATIVE SENSITIVITY FACTORS FOR LANTHANIDES the case of plutonium bearing materials. A number of empirical equations relating RSFs with physical and chemical properties such as ionisation potentials,melting and boiling points, ionisation cross sections,covalent radii etc.of the elements have been put forward in literature(15). Majority of these equations are applicable only to metallic impurities present in the form of elements in the matrix . In the present work however the lanthanides were taken as oxides or nitrates. Hence the above parameters cannot be used for computing the RSF values.

It was seen earlier that the decomposition energies of sesquioxides and bond dissociation energies of the monoxides of the lanthanides explained well the trend observed in the experimentally determined RSF values. It was therefore thought worthwhile to use these themodynamic data for calculating the RSF values using an empirical equation involving the decomposition energy of the sesquioxide or the bond dissociation energy of the monoxide.

Let T_M be the concentration of a lanthanide. As the production of the metal ion is dependent on the decomposition energy of the lanthanide oxides, the relative concentration of the lanthanide with respect to the matrix element can be expressed as a function of the decomposition energy of it's sesquioxide $D_0(M_2O_3)$

$$T_M \;\alpha\; (D_0(M_2O_3))^b$$

or

$$T_M = a(D_0(M_2O_3))^b \qquad \text{-----(6)}$$

where a is a proportionality constant depending on the properties of the matrix element(6). A similar equation can be written for the internal standard Er

$$T_{Er} = a'(D_0(Er_2O_3))^b \qquad \text{------(7)}$$

a=a' since both the elements are being determined in the same matrix. From equations (6) and (7) we have

$$T_M/T_{Er} = D_0(M_2O_3)^b/D_0(Er_2O_3)^b \qquad \text{-----(8)}$$

The left hand side of the equation (8) is the RSF value for the lanthanide trace constituent M with respect to Er internal standard. Thus it can be seen that the RSF values can be expressed as a function of the ratio of the decomposition energies of the lanthanide sesquioxides. A similar equation can be written using the bond dissociation energies of the lanthanide monoxides

$$T_M/T_{Er} = D_0(M\text{-}O)^b/D_0(Er\text{-}O)^b \qquad \text{-----}(9)$$

The RSF values were therefore computed using equations (8) and (9) for different values of the slope b. Table 4 gives the ratios of the decomposition energies of the sesquioxides for b = -2, -1.5 ,-1 , 1 and 2. The best agreement between the experimental and computed RSF values was obtained for the value of the slope b =-1. Table 5 compares the experimentally determined RSF values for lanthanides in U_3O_8 as well as in graphite matrices obtained in the present investigations and also in Y_2O_3 and Al matrices available in literature with the calculated RSF values. It is seen that the computed RSFs are within 20% of the experimental RSFs in all the matrices except for Nd,Sm and Eu in Y_2O_3 determined by Sasamoto etal. It is worth mentioning that the RSF values were determined in the present investigations employing ED system in magnetic peak switching mode and are in better agreement with the computed RSF values than those obtained in the case of Y_2O_3 and Al matrices where photo plate detection system was employed. It should be noted that the RSF values determined by using ED system unlike the photo plate detection system do not require the correction factors to account for the background fog, mass dependent emulsion sensitivity and the line width. It may be expected therefore that the evaporation and ionisation processes occurring in the rf-spark source are mainly responsible for the RSF values. It is further confirmed by the very good agreement among the RSF values in two different matrices U_3O_8 and graphite unlike two sets of different values obtained in Y_2O_3 matrix as seen from table 5.

TABLE 4. Computed RSF values for lanthanides using equation 8 for the various values of slope b. Decomposition energy of sesqui oxides used

Element	Computed RSF values for different slopes (b)				
	b=-2	b=-1.5	b=-1	b=1	b=2
Ce	0.84	0.88	0.92	1.09	1.19
Nd	1.07	1.05	1.04	0.96	0.93
Sm	1.30	1.21	1.14	0.88	0.77
Eu	1.60	1.42	1.27	0.79	0.62
Gd	0.94	0.95	0.97	1.03	1.07
Dy	1.06	1.04	1.03	0.97	0.94
Er	1.00	1.00	1.00	1.00	1.00
Lu	0.86	0.89	0.93	1.08	1.17

TABLE 5. Experimental and computed RSF values for lanthanides (Er as internal standard)

Element	Experimental RSF values					Computed RSF values for b=-1 from	
	U_3O_8 present work	Graphite present work	Y_2O_3 ref 3	Y_2O_3 ref 4	Al ref 5	eqn.8 $\frac{D_0(Er_2O_3)}{D_0(M_2O_3)}$	eqn.9 $\frac{D_0(Er-O)}{D_0(M-O)}$
Ce	0.99	0.74	0.70	0.52	0.96	0.92	0.80
Nd	1.12	1.10	1.63	1.08	0.94	1.04	0.87
Sm	1.23	1.13	1.74	1.43	1.00	1.14	1.07
Eu	1.26	1.15	2.16	1.63	1.16	1.27	1.10
Gd	0.91	0.84	1.10	0.85	1.50	0.97	0.85
Dy	1.06	1.06	1.16	1.10	0.97	1.03	1.00
Er	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Lu	0.88	0.72	0.83	0.79	0.84	0.92	0.85

With Er as internal standard, the computed RSF values for lanthanides can therefore be used to determine the concentration of these elements in other matrices particularly in plutonium bearing fuel materials in view of the nonavailability of trace constituent standards for these materials.

The consistency in the RSF values for lanthanides in various matrices determined employing different experimental conditions and detection systems has clearly brought about the importance of selecting proper internal standard so as to make the RSF values insensitive to all these parameters.

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